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# Inward Cationic Diffusion in Polyvalent Ion-Containing Silicate Glasses

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It is well known that surface characteristics have a strong impact on the physical and chemical properties of glassy materials, and hence, on their applications. In the present work, we modify the surface of polyvalent element containing silicate glasses via new chemical routes, i.e., by using the reduction-inward diffusion approach. We heat-treat the iron or vanadium containing silicate glasses under a flow of  $\text{H}_2/\text{N}_2$  (1/99 v/v) gas at temperatures around the glass transition temperature ( $T_g$ ) to induce redox reactions and internal diffusion processes. The reduction of the polyvalent element occurs by a combination of two processes:  $\text{H}_2$  permeation (dissolution and diffusion) and outward (from interior towards the surface) flux of electron holes. During the reduction of iron or vanadium, hydroxyl (OH) groups form and are incorporated into the glass structure. To maintain charge neutrality, the flux of electron holes requires an inward diffusion of mobile network-modifying cations. As a result of this inward diffusion, a silica-rich nanolayer forms on the glass surface, which increases the hardness and chemical durability. The extent of the cationic diffusion depends on temperature and duration of the heat-treatment. Hence, this new method has potential to be applied in the generation of functional surfaces on glassy materials.

**Keywords:** inward diffusion, reduction, surface modification